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Computerised glow curve deconvolution : the case of 110°C peak of chert

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Abstract : The kinetics of the well known 110°C thermoluminescence (TL) peak of chert (SiO_2) is established by using computerised glow curve deconvolution (CGCD) technique. It has been shown that the peak follows second order (b = 2) kinetics disapproving the first order kinetics model suggested by some workers Arguments are presented in favour of the absence of first order kinetics formalism. Though the actual model seems to be more complex than the simple three parameter kinetics formalism at the present state of CGCD, second order kinetics formalism seems to be a practical answer to the problem.

Keywords : Thermoluminescence, Activation energy, Chert (SiO_2)'

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1. Introduction

Computerised glow curve deconvolution (CGCD) technique has attained a high degree of sophistication with the advent of modern microprocessor controlled data acquisition and management systems. It has become popular to extract trapping parameters (thermal activation energy E, frequency factor s and the order of kinetics b) references to which can be found in two recent papers on CGCD of LiF TLD-100 [1,2]. The computer programmes globally used today essentially use the first order kinetics (b = 1) equation of Randall and Wilkins [3], the second order kinetics (b = 2) equation of Garlick and Gibson [4] or the general order (b not necessarily 1 or 2) kinetics equation of Chen [5]. A readymade computer programme to decode glow curves is available in the book of Chen and Kirsh [6].

The 110°C glow peak in quartz has been subject to numerous investigations [7]. The thermoluminescence (TL) group at Oxford has studied in detail the sensitization (also termed as the pre-dose effect) of the 110°C peak in quartz and developed the predose

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technique for dating details of which can be found in the classic text on TL dating by Aitken [7]. In the literature of TL, sensitization means the change of sensitivity of a sample to a given test dose which results from its exposure to a prior radiation followed by a thermal annealing. The so called 110°C peak does not always occur at 110°C in the sense that depending upon the thermal history of the specimen, it may occur anywhere between ~110 to ~140°C when the heating rate is ~5°C/sec [8]. For lower heating rates, it shifts towards lower temperature region.

In this paper, we have used the computer programme of Chen and Kirsh [6] to deconvolute the 110°C glow peak of chert (a variety of SiO_2). The values of trapping parameters of the 110°C TL peak thus obtained, is compared with those reported by earlier workers. Finally, limitations and potentialities of not only the CGCD method but also the kinetics formalism is discussed, keeping in mind the present rigorous analysis.

2. Experimental

2.1. TL recording system :

All the TL curves are recorded using the commercial recording system model TL 1404 (Indotherm Instruments Pvt. Ltd., Mumbai). The system is capable of providing linear heating at any desired rate that can be varied continuously from 10°C/min to 1000°C/min. The sample can be heated upto 600°C. However in the present case, the sample is heated upto 400°C. The heating rate in most of the cases is 175 to 205°C/min. The glow curves are recorded on a two pen strip chart recorder.

2.2. The material :

Chert is a dense rock composed of one or several forms of silica-opal, chalcedony (microcrystalline fibrous quartz) and microcrystaline quartz. Bedded chert found near the limestone deposit of Ukhrul District of Manipur, is used in the present work. Most of the chert used in the study, are grey to greenish in colour.

The sample is grounded to a size of 100 μ. 5 mg of the sample is used in each glow curve measurement.

Microscopically, the cherts of Ukhrul are very fine, sub-transluscent and composed of many microfossils. XRD pattern of the sample used in the present study, shows that the specimen is essentially α-quartz [9].

2.3. The source of excitation/optical bleaching :

Excitation of chert is done by irradiating it with γ-rays obtained from (Co_{60}) source with dose rate of 0.5 Gy/sec.

Optical bleaching of natural TL is done by illuminating the sample with two beams of laser light obtained from He-Cd laser (10 mW) and Argon laser (200 mW). The former emits at 441.6 nm while the later at 488.0 nm. The laser beams were made divergent with uniform illumination spread in a circular spot of diameter ~1.5 cm.

3. Results

Thermoluminescence (TL) curves of chert are recorded with different treatments of the material. The glow curve specifications along with the peak temperature (*Tm*) and the shape factor (μ_g) determined at fractional intensity (*I/Im*) 0.5 and 0.8 are presented in Table 1.

Table 1. Peak temperature (Tm), shape factor (μ_g) and trapping parameters of the 110°C peak of CHERT

Glow Curve Specifications	Experimental parameters				Trapping parameters		
	Tm (°C)	β (°C/sec)	μ_g (0.5)	μ_g (0.8)	E (eV)	s (/sec)	b
NTL + 15 min. γ-irradiation	105.0	3.37	0.57	0.52	0.814	1.5×10^{10}	2
6 min Laser + 2 hr. γ-irradiation	109.7	3.37	0.52	0.50	0.817	1.2×10^{10}	2
Preheat at 300°C + 15 min. γ-irradiation	98.6	3.38	0.52	0.50	0.821	2.9×10^{10}	2
Preheat at 500°C + 15 min. γ-irradiation	106.6	3.38	0.59	0.54	0.827	2.0×10^{10}	2
Preheat at 700°C + 15 min γ-irradiation	112.4	3.38	0.54	0.50	0.841	2.1×10^{10}	2

It is known that the shape factor of a glow peak provides information about the order of kinetics [5,6]. In case of the 110°C peak chert, μ_g (0.5) varies from 0.52 to 0.59 while that for μ_g (0.8) varies from 0.50 to 0.52. The corresponding theoretical values for second order

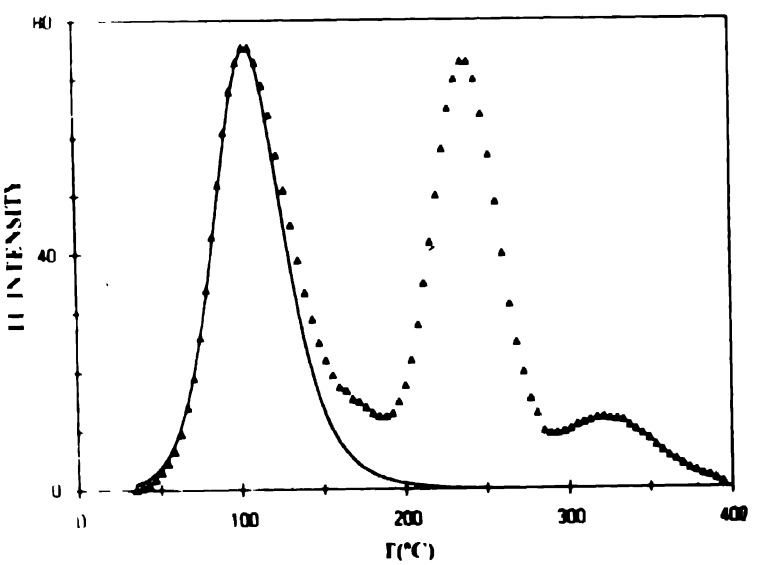

Figure 1. Curve fitting of the 105°C peak of, as obtained, chert (β = 3.37°C/sec) irradiated with γ-rays for 15 minutes. The symbol denotes the experimental data whereas the continuous one is the fitted curve

kinetics TL peak lie in the range of 0.514 to 0.526 and 0.508 to 0.514 [10]. This shows that the peak follows second order kinetics. In the following sections, this has been established by fitting the experimental peaks to numerically generated second order TL peak.

Thermoluminescence (TL) curve of chert irradiated with 15 min. of γ-ray is shown in Figure 1. It shows two prominent peaks at 105 and 239.7°C with additional peaks beyond 300°C. Natural TL (NTL) of this sample is known to exhibit two peaks at 248 and 330°C for heating rate $\beta = 3.33$°C/sec [11]. The glow curve presented in Figure 1 is due to natural radiation received by the material plus the γ-radiation (15 min.). Curve fitting of this peak using the general order kinetics formalism [5,6] shows that the peak fits well to a computed glow curve with $E = 0.814$ eV, $s = 1.5 \times 10^{10}$/sec and $b = 2$. The value of E and s agrees with those obtained by earlier workers (See Table 2) [7,12–14].

Table 2. Trapping parameters of 110°C peak of SiO_2 as reported by earlier workers.

Peak temp. (°C)	Trap depth (eV)	Frequency factor (/sec)	Method of analysis	Reference
110	0.80	2.7×10^9	IR	
110	0.98	8.0×10^{12}	Several techniques	[7]
110	0.99	—	IR, ID, VHR	
~100	0.841		CF ($b = 1$)	
~100	0.855			[11]
~100	0.851			
87	0.871	$\sim 1 \times 10^{13}$	IR	
87	0.881	$\sim 1 \times 10^{13}$	PS	[12]
87	0.999	$\sim 1 \times 10^{13}$	VHR	
90	0.86	$\sim 1 \times 10^{10}$	CF ($b = 2$)	[13]

IR – Initial-rise method PS – Peak shape method. VHR – Various heating rates method
ID – Isothermal decay method CF – Curve-fitting method.

NTL induced in SiO_2 can be destroyed completely by thermal annealing at temperature ≥ 300°C for few hours. Alternately, it can be reduced to a significantly low level by suitable optical bleaching. In the former case the sensitivity changes, depending upon the temperature of heat treatment. In the case of chert, NTL peaks can be practically removed by few minutes (~5 min.) of bleaching with laser light. A sample thus treated is γ-irradiated for 2 hours and TL curve is recorded (Figure 2). The glow curve in this case exhibits two prominent peaks at 109.7 and 222.6°C with additional peaks in the region 300–400°C. Deconvolution of this peak with second order kinetics equation yields $E = 0.817$ eV, $s = 1.2 \times 10^{10}$/sec. The fitting of the numerical curve to experimental one in this case is rather good (Figure 2).

In order to substantiate our result, we have given heat treatment to chert at 300, 500 and 700° C for 4 hours and subject the material (5 mg in each case) to 15 min. of

γ-irradiation. The glow curves recorded under identical conditions are presented in Figure 3. In all the cases, the so called 110°C peak is exhibited quite clearly. As expected with earlier

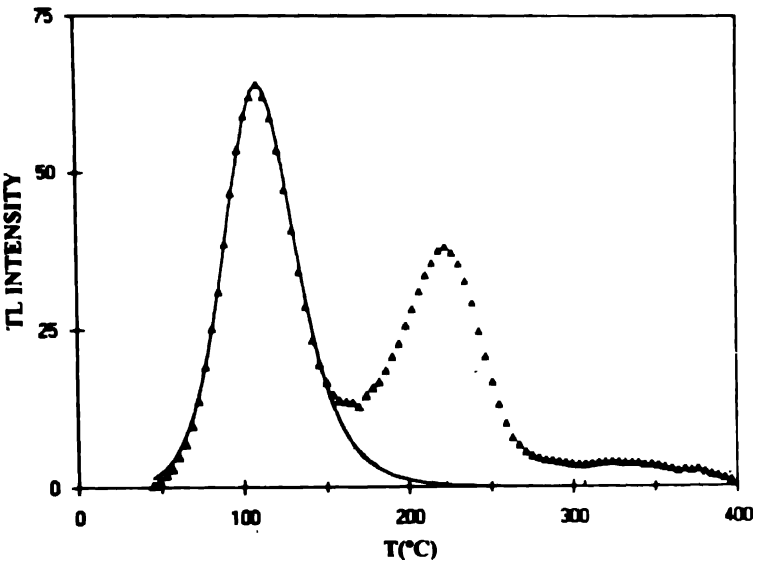

Figure 2. Curve fitting of the 110°C peak of laser bleached (6 min.) chert irradiated with γ-rays for 2 hrs. (β = 3.37°C/sec). The symbol denotes the experimental data and the continuous is the fitted second order peak.

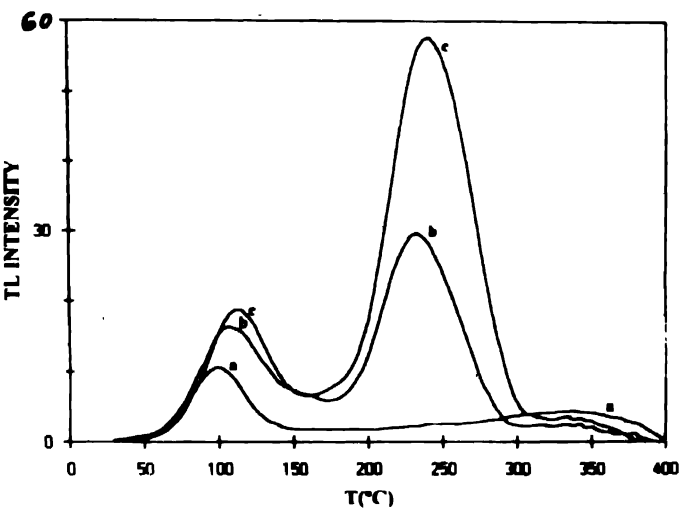

Figure 3. TL glow curve of γ-irradiated (15 min.) chert with preheating at different temperatures (β = 3.38°C/sec). Curves a, b and c are for preheating at temperatures 300, 500 and 700°C.

findings [7], the sensitivity of the 110°C peak increases with the increase of temperature of heat treatment. Further, there is a systematic shifting of the peak temperature with the

increase in peak intensity. Curve fitting of the 110°C peak of Figure 3 shows that it follows second order ($b = 2$) kinetics. The fitting of the numerical curve to the experimental one is

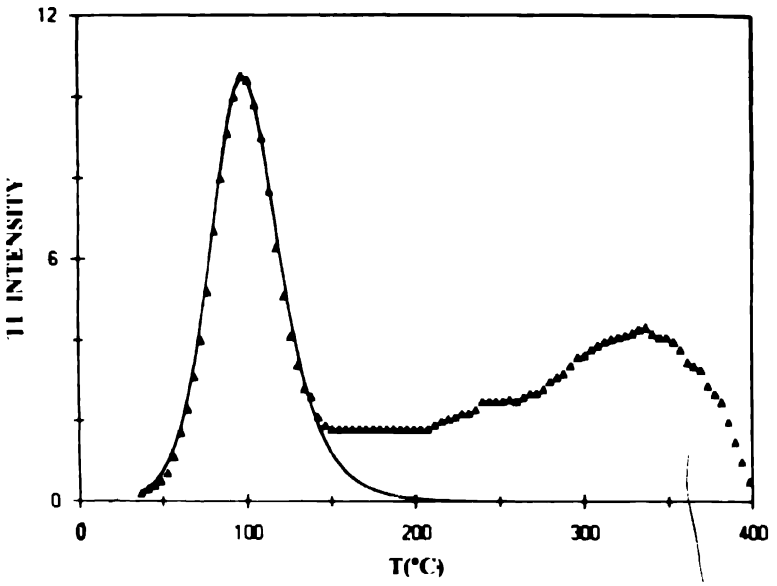

Figure 4. Curve fitting of the first peak of chert preheated at 300°C and irradiated with γ-rays for 15 min The continuous curve is the second order peak and the symbol denotes the experimental curve

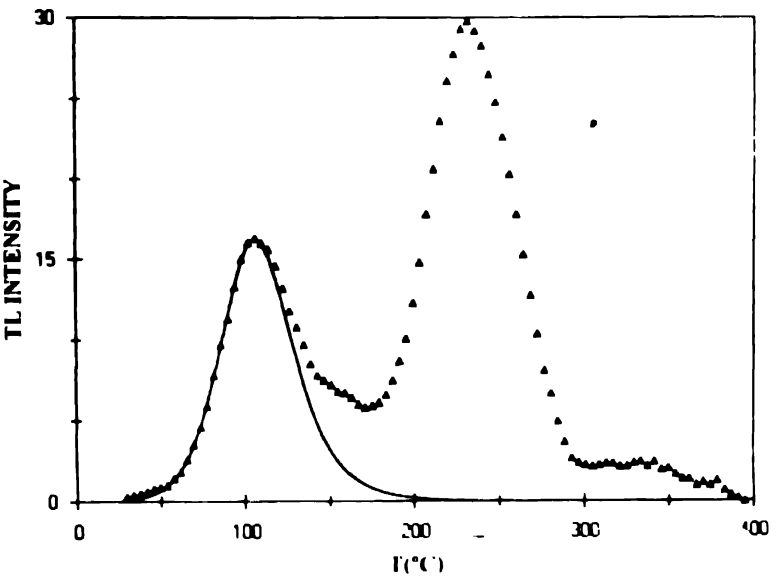

Figure 5. Curve fitting of the first peak of chert preheated at 500°C and irradiated with γ-rays for 15 min The continuous curve is the second order peak and the symbol denotes the experimental curve.

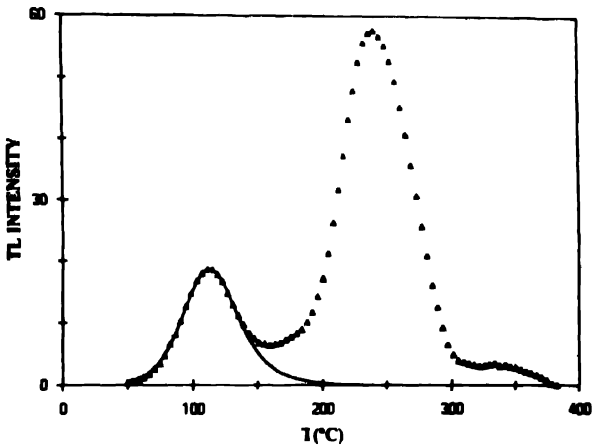

Figure 6. Curve fitting of the first peak of chert preheated at 700°C and irradiated with γ-rays for 15 min. The continuous curve is the second order peak and the symbol denotes the experimental curve.

good in all cases (Figures 4–6). The trapping parameter of the peak for the cases studied here are presented in Table 1.

4. Discussion

4.1. Comparision with earlier results :

The occurrence of TL during a thermal scan of a previously excited material is probably one of the most direct evidence we have for the existance of trapping levels [15]. The glow curve represents a spectrum of energies, each glow peak representing a particular trapping level. The location of a glow peak and its profile provides encoded information of the trapping parameters. Several methods exist in literature to decode the glow curve and retrieve the desired parameters, out of which the computerised glow curve deconvolution (CGCD) may be thought of as the most rigorous, since essentially the total fitting of a glow peak or the entire glow curve provides a mathematical description of the process. The physical basis still remains a matter of speculation since the model used for computation of the numerically generated curves may not represent the actual situation [16]. Within the kinetics formalism, one expects to retrieve three important parameters namely the activation energy (E), the frequency factor (s) and the order of kinetics (b). The present result shows that these parameters as obtained by deconvoluting the 110°C peak of quartz are quite consistent though the peaks are recorded after different thermal/optical treatment of the material.

As far as the kinetics of 110°C peak is concerned, there is no universal agreement, a critical account of which can be found in the review by McKeever [17]. The present result clearly shows that the 110°C TL peak of chert can be best described by second order ($b = 2$) kinetics. Though this is in contrast to the curve fitting result of McKeever *et al* [17] who obtain first order ($b = 1$) kinetics, this agrees with the recent analysis of Kirsh *et al* [14] who

report a second order ($b = 2$) kinetics TL peak at 90°C in silica fibre with $E = 0.86$ eV and $s \sim 1 \times 10^{10}$/sec.

4.2. Physical basis of non-first order kinetics :

Sensitization (pre-dose effect) and superlinear dose dependency are two well documented experimental findings in TL of quartz which has been the topic of many workers [8,18–21]. Neither of the phenomenon can be explained on the basis of first order kinetics model (Figure 7a) where one considers only one kind of trap and one kind of recombination centre

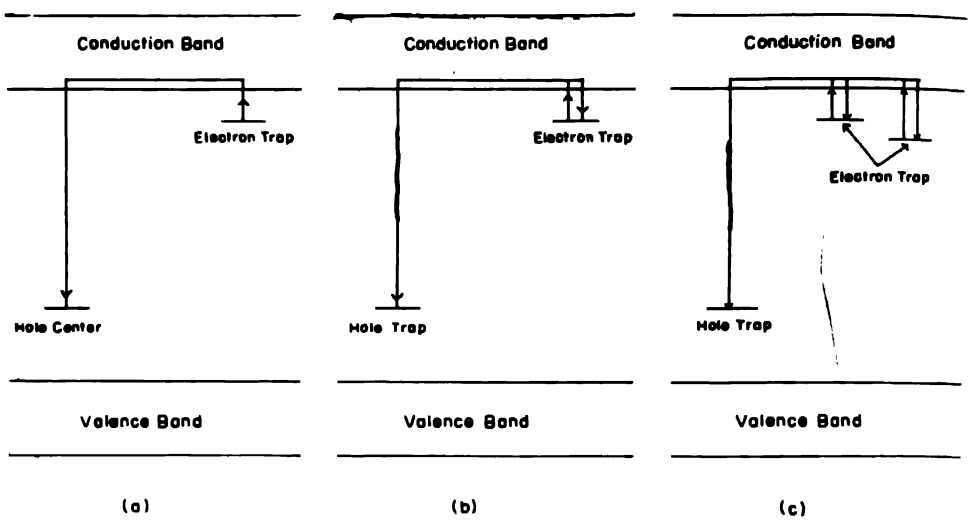

Figure 7. Schematic band model to explain TL (a) Randall and Wilkins model. (b) Garlick and Gibson model. (c) Chen, Fogel and Kristianpoller model.

with negligible retrapping of electron, once they are thermally activated from the trap. In the case of second order kinetics model, one assumes equal recombination and retrapping probabilities. This is depicted in Figure 7b. Sensitization and superlinearity have been explained on the basis of models consisting of two electron traps and one or more recombination centres. Such a model [20] presented to explain experimental results of sensitization and de-sensitization in the 110°C TL peak of quartz is shown in Figure 7c. The parameters used in the model [20] for numerical calculations relevent to the present work are presented in Table 3. In this model, electron released from shallow trap may either be

Table 3. Parameters used for numerical calculation to explain sensitization and desensitization of 110°C peak [20].

Electron trap	Trap depth (eV)	Frequency factor (/sec)
Shallow	0.9	10^{12}
Deep	1.4	10^{12}

recaptured by the competitor deep trap, retrapped by itself again or recombine with a hole in hole trap to emit light. Essentially, in short, the concept of retrapping has to be introduced in order to account for sensitization and desensitization in quartz, a fact which can not be taken into account under the first order kinetics formalism. Though the competing deep trap is absent in the second order kinetics formalism the concept of retrapping which is the basis that distinguishes it from the first order kinetics formalism does exist. Thus, the present analysis by curve fitting (also known as computerised deconvolution in the literature of TL) demonstrating second order kinetics provides a physical basis for the existence of non-first order kinetics in case of 110°C peak of chert (SiO_2). Even the value of E used in the complex model [20], is in agreement with our finding though the value of s differs (see Tables 1 and 3).

5. Conclusion

Computerised glow curve deconvolution of a set of 110°C TL peak of chert obtained after various thermal/optical bleaching of the material clearly shows that it can be described by the second order kinetics equation [4]. The consistent behaviour of the values of activation energy (E) and frequency factor (s) of the set of results justifies the analysis. Further, the concept of retrapping which forms the basis of a common feature in the second order kinetics as well as in the more generalised models where one considers the presence of competing traps to account sensitization and superlinearity in quartz (SiO_2) clearly establishes the fact that in general, first order kinetics in the case of 110°C peak can not be a reality. However, such a possibility under certain specific cases is not ruled out. This requires deconvolution using more complex models, a feat which by no means is straight forward.

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